

Rotational Magnetic Moments of Lithium Hydride and Deuteride*

T. R. LAWRENCE,† C. H. ANDERSON, AND N. F. RAMSEY

Harvard University, Cambridge, Massachusetts

(Received 24 January 1963)

Resonances of the rotational magnetic moments were observed in molecular beams of lithium hydride and lithium deuteride. The shape of the LiH rotational magnetic resonance curve was observed to be asymmetric and the width of the curve was observed to increase with increasing magnetic field. These effects were ascribed to centrifugal stretching causing the magnetic moment per unit of angular momentum to vary with angular momentum. The variation was assumed to be of the form, $\mu_R/J = g_0 + CJ(J+1)$, where μ_R is the rotational magnetic moment and J is the quantum number of the total rotational angular momentum. The values of the constants g_0 and C assigned to LiH were: $g_0 = -0.654 \pm 0.007$ nuclear magneton and $C = (1.2 \pm 0.6) \times 10^{-4}$ nuclear magneton. For LiD, these constants were found to be: $g_0 = -0.272 \pm 0.005$ nuclear magneton and $C = (3.4 \pm 1.7) \times 10^{-5}$ nuclear magneton. The electric dipole moment and its polarity were calculated from the rotational magnetic moments of LiH and LiD. The results of this calculation were $\mu_e = 5.9 \pm 0.5$ debyes with the polarity Li^+H^- . The magnitude of the rotational magnetic moment resonance signals suggest the occurrence of multiple-quantum transitions, which may make possible the observation of rotational magnetic moment resonances in other molecules, even if the rotational gyro-magnetic ratios are quite small.

I. INTRODUCTION

THE LiH molecule contains four electrons, which is the smallest number of electrons in any diatomic molecule except for H_2 , hence, the measurement of its physical properties are important to the development of the theory of diatomic molecules. Many molecular constants of LiH have been obtained from the visible¹ and infrared² spectra, but some of the molecular constants such as those which describe the quadrupole interaction energy, spin-rotation interaction energy, and other small terms in the Hamiltonian can be obtained only from the radio-frequency spectrum. Recently, Kolenkow for the first time successfully produced a molecular beam of LiH and obtained nuclear magnetic resonance spectra for the proton and the lithium nucleus, which were analyzed to obtain the internal interaction energies.³ Previous attempts to produce a molecular beam of LiH were unsuccessful because LiH decomposes at the temperature needed to vaporize enough to produce a beam. The technique by which this difficulty was overcome is discussed later. Wharton, Klemperer, and Gold have also produced a molecular beam of LiH and made precise measurements of the electric dipole moment and the internal interaction energies of LiH in its first rotational state ($J=1$) using electric resonance.⁴

The present report is on the measurement of the rotational magnetic moments of LiH and LiD by molecular beam magnetic resonance.

* This work was partially supported by the National Science Foundation and the Office of Naval Research.

† Present address: The National Bureau of Standards, Washington, D. C.

¹ F. H. Crawford and T. Jorgensen, *Phys. Rev.* **47**, 358 and 932 (1935); **49**, 745 (1936); R. S. Mulliken, *ibid.* **50**, 1017 (1936).

² T. C. James, W. G. Norris, and W. Klemperer, *J. Chem. Phys.* **32**, 728 (1960).

³ R. J. Kolenkow, Ph.D. thesis, Harvard University, 1959 (unpublished).

⁴ L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.* **33**, 1255 (1960).

II. APPARATUS

The molecular beam magnetic resonance apparatus used for this experiment was originally constructed for high-precision measurements of the hydrogen molecules (H_2 , D_2 , and HD). The basic features of this apparatus have been previously described.^{3,5} The modifications that were made to adapt the apparatus for work on lithium hydride are described in the following paragraphs.

The source oven was changed so it could be heated to nearly 1000°K which was necessary to produce sufficient vapor pressure of LiH. The oven was made from a block of stainless steel and was heated with coils of tantalum wire in thin-walled ceramic tubing through holes in the oven block. Knife-edge slits, which were also made of stainless steel, were mounted on the front of the oven. A small diameter stainless steel tube was welded into the back of the oven to let hydrogen gas into the LiH reservoir. The first ovens had eight heating coils, all in the front half of the oven. The oven was later modified by the addition of four heating coils at the back of the oven around the reservoir chamber to obtain better control over the temperature difference between the front and back of oven. This was done for the following reason: If the slits were too hot, the amount of decomposition of lithium hydride would increase; if the slits were too cold, lithium and lithium hydride would condense and clog the slit opening. When the currents in the front and back heating coils were correctly adjusted, the beam of LiH from this oven could easily be maintained at a stable intensity for periods of 8 h or longer.

The beam was detected by surface ionization of the lithium on a hot oxygenated tungsten wire. The tungsten

⁵ H. G. Kolsky, T. E. Phipps, N. F. Ramsey, and H. B. Silsbee, *Phys. Rev.* **87**, 395 (1952); W. E. Quinn, Ph.D. thesis, Harvard University, 1956 (unpublished); N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, England, 1956); and J. T. La-Tourette, Ph.D. thesis, Harvard University, 1957 (unpublished).

TABLE I. Summary of LiH rotational magnetic moment data.

Run	rf current (A)	H (G)	ν_0 (kc/sec)	$ \mu_R/J _p$ (nm)	Signal/noise
A-1	9	3196±1	1550±20	0.6363±0.0060	1.2
A-2	9	3194	1570	0.6447	1.7
B-1	9	3155	1565	0.6444	2.5
B-2	9	3219	1555	0.6357	1.7
B-3	9	4674±1	2274±20	0.6380±0.0060	1.5
B-4	9	4585	2220	0.6352	1.5
C-1	9	4627	2260	0.6407	2.7
C-2	9	4635	2280	0.6453	3.3
C-3	9	4635	2290	0.6482	3.3
C-4	9	4624	2255	0.6395	3.3
C-5	6	4616	2260	0.6423	1.7
C-6	9½	4614	2276	0.6459	3.3
C-7	12	4606	2265	0.6450	4.0
C-8	13	4598	2245	0.6405	3.5
D-1	10	4647	2290	0.6464	5.0
D-2	10	4642	2280	0.6443	6.3
D-3	10	4643	2270	0.6408	5.0
D-4	10	4636	2273	0.6432	6.7
D-5	10	4634	2270	0.6415	6.7
D-6	10	4630	2280	0.6460	7.3
D-7	10	4628	2265	0.6420	7.3
D-8	10	4655	2280	0.6439	6.1
D-9	10	4655	2275	0.6411	6.6
D-10	10	4652	2278	0.6421	6.6

wire that was used as the detector was 0.01 in. in diameter and was manufactured by General Electric Company in a method which avoided the usual large amount of alkali contamination. After flashing the filament briefly at about 2600°K, no background lithium ion current from the tungsten wire was observed. The filament was normally operated at a temperature of about 1450°K and the pressure in the vacuum system was usually about 1.5×10^{-7} mm Hg. Under these conditions the residual oxygen was adequate to oxidize the surface of the tungsten, if the tungsten was clean. The hot tungsten filament was kept straight by the tension of a tungsten spring which was made according to the criteria of Blodgett and Langmuir.⁶

III. EXPERIMENTAL PROCEDURE

The technique by which a beam of LiH was obtained was basically very simple. The oven was heated so the temperature rose constantly and slowly, reaching the operating temperature of about 930°K in about $2\frac{1}{2}$ h. Excess hydrogen was introduced into the oven as soon as it started to heat up and the hydrogen pressure was maintained at about 6 mm Hg throughout the run. In order to avoid flooding the vacuum system with hydrogen, it was necessary to keep the slit opening on the oven small and to have fast pumping on the source chamber. As mentioned earlier, the temperature difference between the front and the back of the oven was as small as it could be made without condensation of beam material on the slit, since the amount of decomposition of the LiH increases rapidly with increasing temperature. The ratio of lithium atoms to lithium hydride molecules

⁶ K. Blodgett and E. Langmuir, *Rev. Sci. Instr.* **5**, 321 (1933).

emerging from the oven was about 100 to 1 in this experiment.

Oven preparation was quite important in this experiment. Before loading the oven, the front of the oven block and the slit jaws were lapped and polished to make them smooth and flat. Also, the edges of the slit jaws had to be sharp, straight, and free of nicks. The pieces were thoroughly cleaned and then the slit jaws were mounted on the oven block, adjusted to a slit width of 0.0003 in., and firmly bolted down. About $\frac{1}{4}$ g of lithium hydride was then put into the oven through a hole which was afterwards sealed with a taper pin plug.

It was necessary to have good thermal contact between the oven block and the slit jaws, otherwise the slit jaws would be cooler than the oven. Even if the slit jaws were not cool enough to condense the beam material, the slit would widen due to the greater thermal expansion of the oven block; 25°C difference in temperature would cause the slit width to double. There are several reasons in addition to the one mentioned earlier for keeping the slit narrow. First, of the molecules undergoing transitions the fraction which is removed from the beam will be further broadened and reduced in intensity by scattering unless the width of the slit is less than the mean free path of the LiH molecules in the vicinity of the slit.⁷ Most of the scattering is due to atomic lithium and molecular hydrogen gas. Thus, for a given slit width, the intensity of the LiH molecular beam is limited by the lithium and hydrogen vapor pressure in the oven, even though Li and H₂ do not contribute to the detected beam. (Atomic lithium is deflected from the beam by the inhomogeneous magnetic field's interaction with the electronic magnetic moment and hydrogen is not detected by the hot wire.)

The deflecting magnets were operated at their maximum gradient of 26 000 G/cm for maximum throw-out power, since the rotational magnetic moment was not expected to be large. The radio-frequency oscillating magnetic field was produced in a coil which was 1 in. long and had four turns. Since the resonance was broadened by internal molecular interactions, a

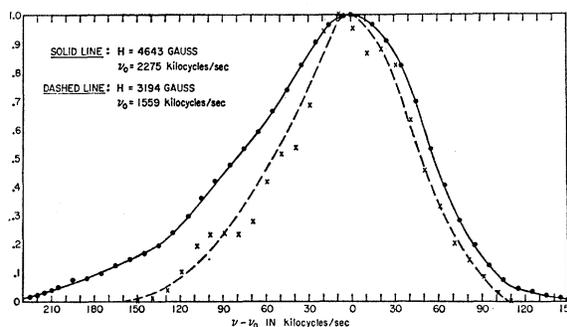


FIG. 1. Averaged resonance curves for LiH rotational magnetic moment at 3194 and 4643 G.

⁷ N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, England, 1956).

short coil was used to provide a broad linewidth and thus increase the magnitude of the resonance signal. The radio-frequency current in this coil was turned on and off at a rate of 17 cps and the modulated portion of the beam signal was amplified in a narrow band amplifier which employed a twin- T feedback loop. The output of the amplifier was converted into a direct current signal in a "lock-in" detector⁸ with an 8-sec time constant filter. This dc signal was then recorded on a moving chart to give a graphic representation of the resonance curve.

IV. EXPERIMENTAL RESULTS

The search for the lithium hydride rotational magnetic moment resonance started with the estimated upper limit of 0.9 nuclear magneton and the frequency of the oscillating field was swept downward as the magnetic field was held constant. When a resonance was found, it was studied at two values of the magnetic field to make sure that the resonant frequency was proportional to the magnetic field strength and, hence, was really the resonance of a magnetic moment. The experimental data are summarized in Table I. The values of the magnetic field were measured using the lithium nuclear moment as a standard.

In order to examine the shape of the resonance curve more closely, the curves were smoothed out and averaged together in accordance with weights given by the signal-to-noise ratio. The averaged curves for the two values of the magnetic field are shown in Fig. 1, and the data from these curves may be summarized as follows:

Magnetic field	3194 G	4643 G
Frequency at peak	1559 kc/sec	2275 kc/sec
Magnetic moment at peak	0.6403 nm	0.6428 nm
Full-width at half-height	103 kc/sec	138 kc/sec
High-frequency half-width	48 kc/sec	57 kc/sec
Low-frequency half-width	55 kc/sec	81 kc/sec

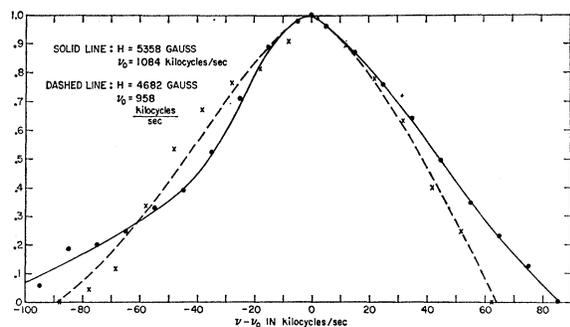


FIG. 2. Averaged resonance curves for LiD rotational magnetic moment at 4682 and 5358 G.

⁸ W. E. Quinn, Ph.D. thesis, Harvard University, 1956 (unpublished).

TABLE II. Experimental LiD rotational moment data.

Run	H (G)	ν_0 (kc/sec)	$ \mu_R/J _p$ (nm)	Signal/ noise
<i>E</i> -1	4682±1	960±20	0.2690±0.0050	2.0
<i>E</i> -2	4682	960	0.2690	2.0
<i>F</i> -1	4687	960	0.2687	2.0
<i>F</i> -2	5353	1075±20	0.2635±0.0050	2.0
<i>F</i> -3	5358	1075	0.2632	2.0
<i>F</i> -4	5357	1090	0.2669	3.0
<i>F</i> -5	5359	1075	0.2632	2.5
<i>F</i> -6	5358	1095	0.2681	2.5
<i>F</i> -7	5358	1090	0.2668	2.5

In spite of a low signal-to-noise ratio, the shape of the resonance curve was noticeably asymmetric. The reason for this asymmetry, as well as the dependence of the width of the resonance curve on magnetic field, is discussed later.

The ratio of the resonance frequency to magnetic field strength is the same within experimental error for both values of the magnetic field; hence, the resonance is shown to be due to a magnetic moment interacting with the external magnetic field. Considering all the data, the magnetic moment corresponding to the peak of the resonance curve is taken to be $|\mu_R/J|_p = 0.6426 \pm 0.0025$ nuclear magneton, where J is the quantum number of the total rotational angular momentum of the LiH molecule.

The experimental data for lithium deuteride were obtained and treated in the same way as for lithium hydride although the signal-to-noise ratio was even smaller than for LiH. The experimental data for two values of the magnetic field are summarized in Table II, and the averaged resonance curves are shown in Fig. 2. Contrasted to the LiH curves, the LiD curves are narrower, the asymmetry is far less pronounced, and there is no observable dependence of width on magnetic field. The averaged data for LiD may be summarized as follows:

Magnetic field	4682 G	5358 G
Frequency at peak	958 kc/sec	1083.5 kc/sec
Magnetic moment at peak	0.2684 nm	0.2653 nm
Full width at half-height	80 kc/sec	80 kc/sec

The magnetic moment corresponding to the peak of the lithium deuteride resonance curve, considering the data for both values of the magnetic field, is taken to be $|\mu_R/J|_p = 0.2662 \pm 0.0020$ nuclear magneton.

V. DETERMINATION OF THE SIGN OF THE ROTATIONAL MOMENTS

In order to determine the signs of the moments, the oscillating radio frequency magnetic field was replaced by a rotating magnetic field. Transitions of the mag-

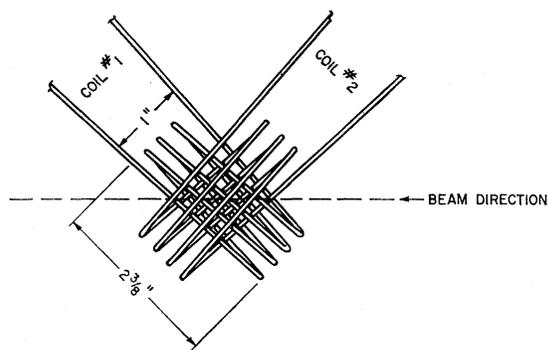


FIG. 3. Diagram of coils used to produce rotating magnetic field. Direction of homogeneous field is perpendicular to plane of paper.

netic moment are produced only when the direction of rotation, as well as the frequency, of the rotating magnetic field is the same as the precession of the magnetic moment in the homogeneous magnetic field. An oscillating magnetic field induces transitions at the resonant frequency whatever the sign of the magnetic moment, since the oscillating field can be considered as the superposition of two rotating fields with equal magnitude and frequency, but opposite directions of rotation. Therefore, the sign of the magnetic moment can be determined directly by observing which direction the magnetic field must rotate in order to produce transitions at the resonant frequency.

The rotating magnetic field for this experiment was produced by the superposition of two oscillating magnetic fields with the same frequency, but differing in phase and spatial orientation by 90° . Two coils, as shown in Fig. 3, were placed in the magnet gap to produce a magnetic field which rotated in the plane perpendicular to the homogeneous magnetic field. Each coil was 1 in. long and made of four turns of 0.080-in.-o.d. copper tubing. Tubing was used so the coils could be cooled by water circulation. Inductance and capacitance were added in series to each coil to make resonant circuits at the frequency of the magnetic resonance. These two resonant circuits were then connected in parallel. The capacitance in one circuit was increased to reduce the current in the coil to $\sqrt{1/2}$ of the current at resonance and the other circuit was detuned by the same amount by decreasing the capacitance. The currents in the two coils were then 90° different in phase, thus, they produced the rotating magnetic field. To reverse the direction of rotation of the magnetic field, each circuit was detuned in the opposite direction.

By observing the resonance signals as a function of the direction of rotation of the magnetic field, it was determined that the sign of the LiH rotational moment was opposite that of the lithium nuclear moment. Since the lithium nuclear moment is positive, the LiH rotational magnetic moment is negative. In the same way, the LiD rotational magnetic moment was found to be negative also. The significance of the negative rotational

magnetic moment is that the largest contribution to the magnetic moment is from the circulation of electrons. This is the opposite of the results obtained for a number of other molecules containing hydrogen, such as H_2 and HF.

VI. DISCUSSION OF RESULTS

The asymmetry of the LiH rotational magnetic moment resonance curve and the dependence of the width on the magnetic field strength, which were mentioned earlier, are probably chiefly due to a variation of μ_R/J with J . The first vibrational state of LiH is not sufficiently excited at the beam temperature to account for the observed amount of asymmetry. Similar variations have been observed in other molecules; precision measurements of the rotational magnetic moment of H_2 showed a slight difference in the values of μ_R/J for $J=1$ and $J=2$.⁹ The variation was explained by including the effect of centrifugal stretching in the theory,¹⁰ which gives the approximate relation $(\mu_R/J) = [g_0 + CJ(J+1)]\mu_{nm}$, where μ_{nm} is one nuclear magneton.

An attempt was made to derive approximate values of g_0 and C from the shape of the LiH resonance shape. It was assumed that the spectrum consisted of a large number of unresolved lines, with each line corresponding to a given value of J , spaced according to $(\mu_R/J) = [g_0 + CJ(J+1)]\mu_{nm}$. Further splitting of the lines was assumed to be negligible compared to the inherent linewidth due to the short length of the oscillating magnetic field. The height of each of the lines in the spectrum was assumed to be proportional to the thermal distribution of rotational angular momenta multiplied by a factor to allow for the possibility of multiple quantum transitions. The probability of multiple quantum transitions increases as J increases, hence, the large values of J are enhanced in the spectrum due to the increased throw-out power accompanying multiple quantum transitions.

Approximate shapes for resonance curves were calculated for various values of g_0 and C . The details of the calculation will not be given here, but they have been presented elsewhere.¹¹ The best fit to the experimental curve was obtained for $g_0 = -0.654 \pm 0.007$ and $C = (1.2 \pm 0.6) \times 10^{-4}$, with the peak of the resonance curve corresponding to $J = 9 \pm 3$. The magnetic moment for the first rotational level is estimated to be $\mu_R(J=1) = -0.654 \pm 0.007$ nuclear magneton. The estimated errors in the values of g_0 and C are large because some of the assumptions that were made to simplify the computation are only qualitatively accurate.

⁹ N. J. Harrick, and N. F. Ramsey, Phys. Rev. **88**, 228 (1952); R. G. Barnes, P. J. Bray, and N. F. Ramsey, *ibid.* **94**, 893 (1954); and W. E. Quinn, Ph.D. thesis, Harvard University, 1956 (unpublished).

¹⁰ N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

¹¹ T. R. Lawrence, Ph.D. thesis, Harvard University, 1961 (unpublished).

The LiD curves did not display enough asymmetry or linewidth to be analyzed in the same way as for LiH. However, if it is assumed that the second moment of the electron charge distribution depends on the internuclear distance according to $\langle e^2 \rangle = \langle e^2 \rangle_0 (R/R_0)^b$, then an approximate value of b can be obtained from the LiH data in the preceding paragraph. If it is further assumed that b is the same for LiH and LiD, then the value of the constant C can be calculated for LiD. The results of the calculations¹¹ are: $b = 1.3 \pm 0.4$ and $C_{\text{LiD}} = (3.4 \pm 1.7) \times 10^{-5}$. Using this value of C an approximate resonance curve was calculated; the peak of which was found to correspond to $J = 13$, approximately. Thus, $g_0 = -0.272 \pm 0.005$ and the magnetic moment of LiD in the first rotational state is $\mu_R (J=1) = -0.272 \pm 0.005$ nuclear magneton.

The value of the constant C that was obtained for LiH is compatible with the value of the electric dipole derivative $\theta = +1.8 \pm 0.3$, which has been obtained from infrared spectral data.² The electric dipole derivative is defined as $\theta = (\mu_0/R_0)/(d\mu/dR)_0$, where R is the internuclear distance, μ is the electric dipole moment, and the subscript zero denotes the equilibrium value. Strictly speaking, no comparison between C and θ should be made, but both quantities indicate that the electron distribution is stretched less by rotation of the molecule than the internuclear distance is stretched. If the first moment of the electron distribution is assumed to vary with internuclear distance as $\langle e \rangle = \langle e \rangle_0 (R/R_0)^{bb'}$, then the value of the electric dipole derivative indicates that $b' = 1.45 \pm 0.22$. This is approximately equal to the value of $b = 1.3 \pm 0.4$ which was obtained from the shape of the LiH rotational magnetic moment resonance curve.

It is interesting to note that a very simple but unrealistic model of the lithium hydride molecule gives the correct value of the magnetic moment. Consider a system of two particles, one with its mass equal to the mass of the proton and its charge equal to $-z_0$ and the other with its mass equal to the mass of the lithium nucleus and its charge equal to $+z_0$, where z_0 is the absolute value of the electric dipole moment divided by the internuclear distance of LiH. The classical calculation of the gyromagnetic ratio for this system gives -0.6582 nuclear magneton, which is equal (within experimental error) to $\mu_R (J=1) = -0.654 \pm 0.007$ nuclear magneton obtained for LiH. Using the same model for gyromagnetic ratio of LiD, one obtains -0.2742 nuclear magneton as compared to $\mu_R (J=1) = -0.272 \pm 0.005$.

VII. CALCULATION OF ELECTRIC DIPOLE MOMENT

The isotopic shifts of rotational magnetic moments have been discussed by Ramsey,^{10,12} Schwartz,¹³ and others.¹⁴ With neglect of small vibrational and centri-

fugal distortion effects, the rotational gyromagnetic ratio of a linear $^1\Sigma$ molecule may be expressed¹⁰ as

$$g = \mu_R / J \mu_N = (M/A) [\sum_i Z_i (R_i - R_z)^2 - (8mc^2/e^2) \sum' | \langle 0 | \sum_k m_{k\sigma c}^0 | n \rangle |^2 / (E_n - E_0) + (\sum_i Z_i) (D^2 - d^2)], \quad (1)$$

where M is the mass of the proton, A is the moment of inertia of the molecule, $R_i - R_z$ is the distance of the i th nucleus with charge eZ_i from the centroid of nuclear charge, $\sum_k m_{k\sigma c}^0$ is the operator⁷ for the electronic orbital angular momentum about an axis perpendicular to the molecular axis and passing through the centroid of the electron distribution. E_n is the energy of the n th excited electronic state, and D and d are the distance from the center of mass to the centroids of the nuclear charge and of the electronic charge, respectively.

Since the electronic configuration is not significantly altered in an isotopic substitution and since the first two terms in the brackets are calculated with respect to axes determined by charge and not mass distributions, these two terms are approximately unaltered under isotopic interchange and may be combined into a single isotopically independent constant. The last term in the brackets may be replaced by

$$(\sum_i Z_i) (D^2 - d^2) = (1/e) (D+d) [e(\sum_i Z_i) (D-d)] = (1/e) (D+d) \mu_e, \quad (2)$$

where μ_e is the electric dipole moment of the molecule. With these changes Eq. (1) may be written as

$$g = (M/A) [G + (D+d) \mu_e / e]. \quad (3)$$

Hence, if the g 's of two molecules, a and b , differing only in isotopic composition are measured,

$$g_b - (A_a/A_b) g_a = (M/eA_b) (D_b + d_b - D_a - d_a) \mu_e = -2M \mu_e \Delta X / eA_b, \quad (4)$$

where $\Delta X = D_1 - D_2 = d_1 - d_2$ is the displacement of the center of mass of the molecule under isotopic interchange.

Since the moments of inertia of LiH and LiD are known,¹⁵ the electric dipole moment of the molecule can be calculated from Eq. (4) and from the above measured values of the rotational magnetic moments with the result that

$$\mu_e = -5.9 \pm 0.5 \text{ D.}$$

The magnitude of this result is in good agreement with the more precise determination of Wharton⁴ that $|\mu_e| = 5.882 \pm 0.003$ D. The sign of μ_e is measured for the first time in this experiment.

The significance of the minus sign is that the electric dipole is pointing in the opposite direction from the direction of the displacement of the center of mass when the hydrogen nucleus is replaced by the deuterium

¹² N. F. Ramsey, Phys. Rev. **58**, 226 (1940).

¹³ R. Schwartz, Ph.D. thesis, Harvard University, 1952 (unpublished).

¹⁴ C. H. Townes and A. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

¹⁵ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., New York, 1950).

nucleus. The center of mass is shifted from the lithium nucleus when the proton is replaced by the deuteron. Therefore, the electric dipole is pointing toward the lithium nucleus, which means that the lithium is positive and the hydrogen is negative. This polarity agrees with the theoretical expectation, but there has been no previous experimental proof that this polarity was correct.

The good agreement between the magnitude of the electric dipole moment obtained in this way with the electric resonance experimental value is encouraging. The magnitude of the electric dipole moment calculated from Eq. (4) is very sensitive to errors in the magnetic moments, which confirms that the rotational magnetic moments are probably correct within the stated error. It is also an indication of the validity of Eq. (4).

VIII. MULTIPLE QUANTUM TRANSITIONS

Besides providing values of the LiH and LiD rotational magnetic moments, the experiment indicated that the molecular beam magnetic resonance method might be applicable to the measurement of even quite small rotational gyromagnetic ratios in other molecules. The temperature and moment of inertia are usually such that a significant number of the molecules in a beam are excited to rotational states of large quantum number (large J), and multiple quantum transitions can occur if the m_J energy levels are evenly spaced and if the perturbing magnetic field is strong enough.^{7,16-18} The multiple quantum transitions increase the size of the resonance signal because the deflection produced by the inhomogeneous magnetic fields is proportional to $(\mu_R/J)\Delta m_J$.

The occurrence of multiple quantum transitions in this experiment was demonstrated by comparing the size of the LiD rotational magnetic moment resonance signal with the deuteron resonance signal in LiD. If only $\Delta m = \pm 1$ transitions are considered, the estimated throwout power for the deuteron moment is about seven times as large as that for the LiD rotational moment.

However, the observed resonance signal for the deuteron was only two times the observed resonance signal for the LiD rotational moment, which indicated that transitions with $\Delta m > 1$ did occur in the latter resonance. The LiD rotational magnetic moment resonance signal would probably have been significantly increased if the oscillating magnetic field had been increased. However, the maximum current from the radio equipment that was used produced a perturbing magnetic field which was about one-fourth of the optimum for producing $J=1$, $m_J=0 \leftrightarrow J=1$, $m_J=1$ transitions of the LiD rotational magnetic moment.

A molecular beam magnetic apparatus to use multiple quantum transitions to full advantage in the measurement of small rotational gyromagnetic ratios would have the following features: The perturbing field should be short enough that the variation in the spacing between energy levels of successive m_J is smaller than the inherent linewidth associated with the length of the oscillating field. The magnitude of the oscillating field should be large enough to precess the rotational angular momentum approximately 180° .

IX. CONCLUSIONS

The rotational magnetic moments of LiH and LiD have been measured and found to have the magnitudes and signs given in Sec. VI above. From these results the magnitude of the electric dipole moment of lithium hydride is obtained and the sign of the electric dipole moment is found to be positive, in agreement with theoretical expectations. The observed asymmetry of the resonance curves can be analyzed in terms of the centrifugal stretching of the molecule.

Multiple quantum transitions were observed in the experiment. In future experiments of this nature, it should be possible deliberately to use multiple quantum transitions to measure rotational magnetic moments of molecules whose gyromagnetic ratios are much too small for single quantum transitions to be detectable with the deflecting power of a typical molecular beam apparatus.

The authors would like to thank Dr. W. Klemperer and Dr. L. Wharton for helpful suggestions concerning the production of LiH.

¹⁶ P. Kusch, Phys. Rev. **93**, 1022 (1954); **101**, 627 (1956).

¹⁷ J. M. Hendrie and P. Kusch, Phys. Rev. **107**, 716 (1957).

¹⁸ J. Pinkerton, Ph.D. thesis, Harvard University, 1961 (unpublished).